This Page Is Inserted by IFW Operations and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

THIS PAGE BLANK (USPTO)

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7: (11) International Publication Number: WO 00/38621 A61K 7/00, 7/06 A1 (43) International Publication Date: 6 July 2000 (06.07.00) (72) Inventors: BERGMANN, Wolfgang, Robert; Unilever Home (21) International Application Number: PCT/EP99/10168 & Personal Care Usa, 325 North Wells, Chicago, IL 60610 (US). JANCHITRAPONVEJ, Ben; Unilever Home & (22) International Filing Date: 15 December 1999 (15.12.99)

US

(71) Applicant (for AE AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT TZ UG ZA ZW only):

23 December 1998 (23.12.98)

UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

- (71) Applicant (for all designated States except AE AU BB CA CY GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT TZ UG ZA ZW): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).
- (71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

- Personal Care Usa, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). EVANS, Trefor, Unilever Home & Personal Care Usa, 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US).
- (74) Agent: GRIFFITHS, Helen, Sarah; Unilever PLC, Patent Dept., Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).
- (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: SELF-WARMING HAIR CONDITIONING COMPOSITIONS

(57) Abstract

(30) Priority Data:

09/220,475

An essentially anhydrous hair conditioning composition comprising: (a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule; (b) carrier molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials; and (c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials. The invention also relates to a method for conditioning hair with warming which comprises administering to the hair, with water, the hair conditioner compositions of the invention.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
ΑU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece :	•	Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
·CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		•
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
cz	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

- 1 -

SELF-WARMING HAIR CONDITIONING COMPOSITIONS

FIELD OF THE INVENTION

5

This invention concerns processes and compositions for the treatment of human hair. More particularly the invention concerns a hair conditioner composition and a conditioning shampoo composition that provide a noticeable increase in temperature during use and that provide good conditioning properties to the hair.

BACKGROUND OF THE INVENTION AND PRIOR ART

15

20

2.5

30

10

When treating hair with conditioner, it would be desirable for the conditioner being used to increase in temperature during actual use. More specifically it would be desirable for the conditioner to increase in temperature after being added to hair that is already wet (for example, after shampooing). Alternatively such a conditioner could be added to dry hair and then after water is added, there would be an increase in temperature in said conditioner. Finally, such a conditioner could be put on hair simultaneously with water and the conditioner would increase in temperature. Such increases in temperature are referred in this specification as self-warming. Such self-warming would provide the consumer with a feeling of comfort and relaxation, as well as supplying the consumer with a "signal" that the conditioner composition is working.

- 2 -

A self-warming composition which is presently on the market is Lux Super Rich Self Warming Conditioner. It is an anhydrous glycol containing composition which generates heat through the dissolution of the glycol in water. By contrast the compositions of the present invention generate heat when water adsorbs into the pores of the microporous materials. Anhydrous glycol containing products increase in temperature on application of water, 7 to 8 degrees C under normal conditions of use on the hair. The compositions of the present invention will often increase in temperature significantly more upon application of water during use in the hair.

It is an object of the present invention to provide an improved hair conditioner which provides increased self-warming hair conditioner composition during use (i.e., when applied to hair with water) while not decreasing the conditioning provided, and in some cases increasing the conditioning that is provided.

20

10

BRIEF SUMMARY OF THE INVENTION

The invention relates to hair conditioner compositions which are essentially anhydrous that comprise:

- (a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule;
- 30 (b) carrier molecules or molecular aggregates that have critical diameters larger than the largest

- 3 -

average pore size of the microporous materials; and

(c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials.

The invention also relates to a process for treating hair which comprises administering to said hair, the hair conditioner composition described above.

10

5

The invention also relates to a conditioning shampoo composition that provides a noticeable increase in temperature during use.

The invention also relates to a process for treating hair which comprises administering to said hair, the conditioning shampoo composition described above.

The hair conditioner compositions of the invention and the

conditioning shampoo compositions provide increased selfwarming during use (i.e., when applied to hair with water)
while not decreasing the hair conditioning provided and in
some cases increasing the hair conditioning provided. This
is an unexpected result, since the hair conditioner

compositions of the invention comprise microporous materials
such as molecular sieves which are a solid particulate
material which would be expected to decrease the
conditioning properties of the compositions of the invention
as compared to compositions without microporous materials or
molecular sieves. In fact the compositions of the invention

- 4 -

have the same or increased conditioning properties as noted above.

5 DETAILED DESCRIPTION OF THE INVENTION

20

25

Hair conditioner compositions of the invention include rinse-off and leave-in conditioners.

10 As used herein "essentially anhydrous" means less than about 2 weight % preferably less than about 1 weight % of water.

Unless other indicated, as used herein % means weight %. All of the starting materials described herein are either known or can be prepared according to known methods. The essentially anhydrous hair conditioner compositions of the invention comprise:

- (a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule;
 - (b) carrier molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials; and;
 - (c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials.
- 30 It is noted that each of the one or more microporous materials referred to above has an average pore size larger

- 5 -

than the critical diameter of a water molecule. The size of a water molecule is about 3.2 Angstroms. It is also noted that microporous materials with an average pore size of 3 Angstrom are used in compositions described below. Even though some of such microporous materials have too small a pore size to adsorb water, enough of such microporous materials have a large enough pore size to be useful in the compositions of the invention.

The microporous materials may be selected from the group consisting of inorganic salts such as crystalline metal silicates such as sodium potassium aluminum silicate, aluminum silicate, calcium aluminum silicate, activated alumina (aluminum oxide), clays which are silicates, known as diatomaceous silicas, bentonites and clays these are aluminum oxides and silicon oxides, and crystalline metal aluminosilicates. Among the crystalline metal aluminosilicates which may be employed are aluminosilicates which range in average pore size from about 3 Angstroms to about 10 Angstroms.

In general, the average pore size for the sieves that are used in the compositions of the invention can range from about 3 Angstroms to about 13 Angstroms or larger. more preferably, the average pore size of the sieves can range from about 3 Angstroms to about 1 0 Angstroms.

25

30

The tradenames of these aluminum silicates include Aldrich 3A Sieves, Aldrich 1 OX Sieves, and Sylosiv A3 Sieves, and Sylosiv A4 Sieves.

- 6 -

PQ Corporation is another molecular sieve supplier and the material that they supply, is an aluminosilicate is called Advera 401 N.

- Organic resins such as activated charcoal may also be employed where the average pore size of the organic resins meets the parameters described above.
- The microporous materials are normally present in a

 10 concentration of from 5% to 60%, preferably from 1 0 to 40%

 by weight based on the total weight of the hair treatment

 composition, or more preferably 15 to 30% by weight based on

 the total weight of the hair treatment composition.
- 15 Carrier materials must have a critical diameter larger than the largest average pore size of the microporous materials selected. With respect to the resulting anhydrous hair care composition, as long as most of the pores in the microporous material are unoccupied there will be a heating effect on the addition of water.

The selected carrier materials have to be water soluble or water dispersible otherwise they could not be used on hair in combination with water.

Suitable carrier materials include hydrophilic glycols, polyethylene glycols, and polar solvents like alcohols. Any carrier used must either be water soluble or water dispersible.

- 7 -

The following list of hydrophilic glycols or polyhydric alcohols which may be used in compositions of the invention is meant to be illustrative and not limiting. These hydrophilic glycols are as follows: propylene glycol, ethylene glycol, glycerin, sorbitol, butanediol, butylene glycol, and mixtures thereof.

The following list of polyethylene glycols which may be used in compositions of the invention is meant to be illustrative and not limiting. These polyethylene glycols are as 10 follows: PEGs -4, -6, -8, -9, -10, -12, -14, -16, -18, -20, -200, -400 and -600. Also included are beheneth -5 and -10, peg-7 betanaphthol and PEG-15 butanediol. Also included are buteth-3 carboxylic acid, butoxynol-5 and -19, PEG-8 C12-18 ester, C12 13 pareth-7 carboxylic acid, Cl 1 -1 5 pareth-7 15 carboxylic acid, Cl 2 -15 pareth-7 carboxylic acid, Cl4 -15 pareth-8 carboxylic acid, PEG-8 caprate, PEG-8 caprylate, PEG-8 caprate/caprylate, PEG -6, and -8 caprylic/capric glycerides, capryleth -6 and -9 carboxylic acids, ate, PEG-8 caprylate. Also included are ceteareth -2, -3, -4, -5, -5, 20 -6, -7, -8, -10, , -11, -12, -13, -15, -6, -17, -18, and -20; choleth -1 0 and -20; PEG-3 cocamide, PEG-5 cocamide, PEG-6 cocamide, PEG-7 cocamide, PEG-1 1 cocamide, PEG-20 cocamide; PEG-2 cocamine, PEG-3 cocamine, PEG-5 cocamine, PEG-10 cocamine, PEG-15 cocamine, and PEG-20 cocamine; PEG-5 25 cocoate, PEG-8 cocoate, PEG-1 5 cocoate; coceth-3, 5, and -8; PEG-2 dilaurate, PEG-4 dilaurate, PEG-6 dilaurate, PEG-8 dilaurate, PEG-12 dilaurate, PEG-20 dilaurate, PEG-4 dioleate, PEG6 dioleate, PEG-8 dioleate, PEG-1 0 dioleate, PEG-1 2 dioleate, and isosteareth-2, isosteareth-3, 30 isosteareth-10, isosteareth-12, and isosteareth-20;

- 8 -

isoceteth-10, and -20; isodeceth -4, -5, and -6; isostereath -2, -3, 10, -12, and -20; PEG-3 lauramine oxide; PEG-2 laurate, PEG-4 laurate, PEG-6 laurate, PEG-8 laurate, PEG-9 laurate, PEG-10 laurate, PEG-12 laurate, PEG-14 laurate, and PEG-20 laurate; laureth -1, -2, -3, -4, -5, -6, -7, -8, -9, -10, -11, -12, -13, -14, -15, -16, and -20; oleth 2, -3, -4, -5, -6, -7, -8, -9, -10, 12, -15, -16, and -20; stereath -2, -3, -4, -5, -6, -7, -10, -11, -13, -1 4, -15, -16, and -20; and trideceth -3, -5, -6, -9, -10, -11, -12, and -15.

10

15

20

25

The following list of polar solvents like alcohols which may be used in compositions of the invention is meant to be illustrative and not limiting. These polar solvents like alcohols are as follows: methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol and isopropanol and mixtures thereof.

Carrier materials may be included in compositions of the invention in a weight % range of about 40% to about 90%, more preferably about 60 to about 80%.

Conditioner materials are selected from the group consisting of quaternary ammonium compounds, amidoamines, silicones, cationic polymers, hydrocarbons, fatty alcohols, either alone or in combination. Any conditioner material which is used in a composition of the invention must have a critical diameter that is larger than the largest pore average size of the microporous materials.

30 The following list of silicones which may be used in compositions of the invention is meant to be illustrative

- 9 -

and not limiting. These silicones are as follows: a polyalkyl siloxane, a polyaryl siloxane or a polyalkylaryl siloxane.

- Mixtures of volatile silicones as cyclotetrasiloxane, 5 cyclopentasiloxane, or cyclohexasiloxane are useful. Mixtures of the nonvolatile silicone compounds are also useful. The so-called "rigid silicones", as described in U.S. Patent 4,902,499, herein incorporated by reference, having a viscosity above 600,000 cs at 20C and a weight 10 average molecular weight of at least about 500,000, also are useful in compositions of the present invention. A phenyltrimethicone also is useful as a nonvolatile silicone compound. Also useful is a mixture of a low molecular weight silicone fluid and a higher molecular weight silicone 15 Silicones which are useful in compositions of the invention are described in US patent 5,656,280 which is hereby incorporated by reference.
- Non-volatile silicones include siloxane or siloxane mixtures having a viscosity of greater than 1 0 centistokes.

 Nonlimiting examples include dimethicone, dimethiconol, amodimethicones, phenyl trimethicone and silicone copolyols.
- The following list of cationic polymers which may be used in compositions of the invention is meant to be illustrative and not limiting. These cationic polymers are as follows:

 Guar hydroxypropyltrimonium chloride,

 poly(dimethyidiallylammonium chloride), poly(dimethyl

 butenyl ammonium chloride) bis (triethanolammonium chloride), Poly

~ 10 -

(methyl-beta propaniodiallylammonium chloride), Poly (diallylpiperidinium chloride), Poly (vinylpyridinium chloride), quaternised poly (vinyl alcohol), quaternised poly (dimethylaminoethylmethacrylate) and mixtures thereof. These cationic polymers are described in U.S. Patent 5,580,550 which is hereby incorporated by reference.

The following list of hydrocarbons which may be used in compositions of the invention is meant to be illustrative and not limiting. These hydrocarbons are as follows: nonane, octane, heptane, tert-pentane, dodecane, decahexane, decane, heptadecane, trimethylheptane, trimethylhexane, 4-methylheptane, 4-methyldecane, isobutane, isopentane, isooctane, hexane, isododecane, polydecene, mineral oil, paraffin wax and isohexadecane. Other exemplary volatile hydrocarbons are depicted in the general structural formula I wherein n ranges from 2 to 5.

 $H_3C(C(CH_3)_2-CH_2)_n-CH(CH_3)_2$.

20

25

30

15

5

10

Another exemplary hydrocarbon is ISO-PAR M (a Cl 3-Cl 4 isoparaffin available from Exxon Chemical Co. Baytown Texas). These compounds are described in U.S. Patent 5,656,280 which is hereby incorporated by reference. Also included among volatile hydrocarbons which can be used in compositions of the invention are mineral oil, paraffins, fatty acids, caprylic/capric triglyceride, caprylic/capric diglyceryl succinate, propylene glycol dicaprylate/dicaprate, mineral jelly, acetylated lanolin, Mquat 40, oil soluble lipo-protein, collagen/lanolin oil blend, mineral oil and lanolin alcohol, cetyl acetate,

PCT/EP99/10168 WO 00/38621

- 11 -

lanolin oil, isopropyl palmitate and lanolin oil, silk powder, decyl neopentanate, jojoba oil, and propoxylated polyol.

The following list of quaternary ammonium compounds which 5 may be used in compositions of the invention is meant to be illustrative and not limiting. These compounds have the general structural formula: N[R 1 R2R3R4] + X-where R, is an alkyl group including from about 8 to about 18 carbon atoms, R2 is selected from the group consisting of an alkyl group 10 including from about 8 to about 18 carbon atoms, a hydrogen atom, a methyl group, an ethyl group, a hydroxymethyl group and a hydroxyethyl group, R4 is selected from the group consisting of a hydrogen atom, a methyl group, an ethyl group, a hydroxymethyl group, and a hydroxyethyl group; and 15 X is an anion. The quaternary nitrogen of the quaternary ammonium compound can also be a component of a heterocyclic moiety such as morpholine or pyridine. The anion can be an anion such as chloride, methosulfate, ethosulfate. nitrate, bromide. tosylate. acetate or phosphate. 20

The quaternary ammonium compounds have one or two long chain alkyl groups having from about 8 to about 18 carbon atoms. the long chain alkyl groups can also include in addition to, or in replacement of carbon and hydrogen atoms, ether linkages or similar water solubilizing linkages the remaining two or three substituents of the quaternary nitrogen can be hydrogen or benzyl; or short chain alkyl or hydroxyalkyl groups such as methyl ethylhydroxymethyl or 100 hydroxyethyl groups, or combinations thereof either diether of the same or different identity.

15

Exemplary quaternary ammonium compounds include but are not limited to lauratrimonium chloride, quaternium -16, lauralkonium chloride, dicetyldimonium chloride, cetylpyridinium chloride, soyatrimonium chloride, mytrimonium chloride, cetrimonium chloride, PEG-2 cocomonium chloride, PEG 2 cocoyl quaternium -4, PEG 2 oleyl quarenium 4 polyquaternium -6,-7, -11, -5, -24, and mixtures thereof. these quaternary ammonium compounds are described in U.S Patent 5,656,280 which is hereby incorporated by reference.

Other water-soluble ammonium compounds include distearyl dimonium chloride, and behenyl trimmonium chloride.

The following list of amidoamines which may be used in compositions of the invention is meant to be illustrative and not limiting. These amidoamines Include those described in U.S. Patent 5,328,685 which is hereby incorporated by reference.

Amidoamines include but are not limited to

20 diethylaminoethylstearamine, isosteamidopropyldimethylamine,
cocamidopropyldimethylamine, ricinoleamido
propyldimethylamine, oleamidopropyldimethylamine,
behenamidopropyldimethylamine,
palmitamidopropyldimethylamine, stearamidoethyldiethylamine,

25 stearamidylpropyldiethylamine, stearamidopropyldimethylamine
soyamido propyldimethylamine and dimethylaminopropyl
myristamide.

The following list of fatty alcohols which may be used in compositions of the invention is meant to be illustrative and not limiting. These fatty alcohols include a fatty

- 13 -

alcohol or fatty acid, or derivative thereof, or a mixture of any of these having a chain length of from about 8 to about 36 carbon atoms. More preferably from about 12 to about 22 carbon atoms. These materials may be predominantly linear or may be branched. Preferred are stearyl alcohol, cetyl alcohol, behenyl alcohol, lauryl alcohol, myristyl alcohol, and coco alcohol.

Conditioner materials may be included in compositions of the invention in a weight per cent range of about 2% to about 45%, more preferably about 10 to about 30%.

Optional ingredients which can be used in compositions of the invention are now described.

15

20

25

5

Nonionic surfactants suitable for use in compositions of the invention include condensation products of aliphatic C8-Cl8 primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide, and generally having from 6 to 30 ethylene oxide groups.

Other suitable nonionics include mono- or di-alkyl alkanolamides. Examples include coco mono- or diethanolamide and coco mono-isopropanolamide. Further suitable nonionic surfactants are the alkylpolyglycosides (APG's). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups.

30 Amphoteric and zwitterionic surfactants suitable for use in compositions of the invention may include alkyl amine

10

15

oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinates, alkyl carboxyglycinates, alkyl amphopropionates, alkylamphoglycinates alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms.

Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

Further surfactants which may be suitable for use in conditioning shampoos in accordance with the invention include one or more anionic surfactants instead of or in addition to any of those surfactants mentioned above. Those surfactants must be dispersed or mixed in glycols, PEGS, etc.

Suitable anionic surfactants are the alkyl sulphates, alkyl 20 either sulphates, alkaryl sulphonates, alkaroyl isethionates, alkyl succinate, alkyl sulphosuccinates, Nalkoyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpho-olefin sulphonates, especially their sodium, magnesium, ammonium 25 and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from one to 1 0 ethylene oxide or propylene oxide units per molecule, 30 and preferably contain 2 to 3 ethylene oxide units per molecule.

PCT/EP99/10168 WO 00/38621

- 15 -

Examples of suitable anionic surfactants include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauroyl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine lauryl sulphate 1 E0, 2E0 and 3E0, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1 E0, 2E0 and 3E0.

As further optional components for inclusion in the compositions of the invention, the following may be mentioned: pH adjusting agents, viscosity modifiers, cosmetic fillers such as talc, kaolin; pearlescers, opacifiers, suspending agents, preservatives, coloring agents, dyes, proteins, herb and plant extracts, polyols and other moisturising.

15

30

20 Compositions of the invention can be made by using processes which are which are known in the art or by using processes which are analogous to those known in the art. Compositions of the invention can be made by using starting materials which are known in the art or by using starting materials which are obtainable from materials that are known in the art.

Compositions of the invention are used in a manner known for leave-in and wash-out conditioners. Namely, the hair is wet and then conditioner or conditioning shampoo is applied to the hair.

- 16 -

If the conditioner is a leave-in conditioner, it can be applied to wet or dry hair. If applied to dry hair, then water is added after such application. If the conditioner is a wash-out conditioner, the hair is the rinsed after application.

The self-warming that occurs with the use of the hair conditioner compositions arises when water molecules adsorb into the pores of the microporous materials. This step releases heat which is felt as self-warming. Up to a 170C increase or more, typically increases of 150C or more are achieved with compositions of the invention. 120C increase or more, or increases of 100C or more can also be achieved with compositions of the invention. The temperature increase, being referred to above, which is caused by compositions of the invention is the change which occurs in degrees C when 70 parts of composition is mixed with 30 parts water at room temperature.

20 Compositions of the invention are made by processes known in the art, or analogous to those known in the art using starting materials which are known in the art.

Ingredients which are used in compositions of the invention may fall within the following ranges of weight ratios:

- 17 -

INGREDIENT	WEIGHT %
Microporous materials	5-60
Carrier ingredients	20-80
	1 - 20
Conditioner ingredients	1-30

Examples of the invention shown below are made by processes known in the art, or analogous to those known in the art.

5

Examples of the invention are as follows:

EXAMPLE 1 -- COMPARATIVE EXAMPLE

10 or other microporous materials

Conditioner -- without molecular sieves

15

INGREDIENT	WEIGHT %
PEG 200	71.15
CETEARYL ALCOHOL	2.5
BEHENTRIMONIUM CHLORIDE	2.0
STEARETH-2	1.0
STEARETH-21	1.0
GLYCERIN	18.6
PANTHENOL	0.1
DIMETHICONE	3.0
FRAGRANCE	0.65

Example 2-- Conditioner with molecular sieves or microporous
material

INGREDIENT	WEIGHT %
PEG 200	50.45
CETEARYL ALCOHOL	2.5
BEHENTRIMONIUM CHLORIDE	2.0
STEARETH-2	1.0
STEARETH-21	1.0
PANTHENOL	0.1
GLYCERIN	18.6
CITRIC ACID	0.7
DIMETHICONE	3.0
SODIUM POTASSIUM ALUMINO-	20.0
SILCATE 3 Angstroms	
FRAGRANCE	0.65

- 19 -

Example 3- conditioner with molecular sieves or microporous materials

INGREDIENT	WEIGHT %
PEG 200	55.45
CETEARYL ALCOHOL	2.5
BEHENTRIMONIUM CHLORIDE	2.0
STEARETH-2	1.0
STEARETH-21	1.0
GLYCERIN 99.7%	18.6
PANTHENOL	0.1
CITRIC ACID	0.7
DIMETHICONE	3.0
SODIUM POTASSIUM ALUMINO	15.0
SILICATE 3 Angstroms	
FRAGRANCE	0.65

- 20 -

Example 4--conditioner with microporous materials or sieves

INGREDIENT	WEIGHT %
PEG 200	51.15
CETEARYL ALCOHOL	2.5
BEHENTRIMONIUM CHLORIDE	2.0
STEARETH-2	1.0
STEARETH-21	1.0
GLYCERIN 99.7%	18.6
PANTHENOL	0.1
DIMETHICONE	3.0
SODIUM POTASSIUM ALUMINO	20.0
SILCATE 3 Angstroms	
FRAGRANCE	0.65

100000 JHO 00000144

- 21 -

Example 5

Self-warming Shampoo can be prepared with ingredients in the following ranges:

INGREDIENT	WEIGHT %
PEG -200	Qs to 1 00
DIMETHICONE	.5 TO 1
SILICA	.1 to 5
GUAR HYDROXYPROPYLTRIMONIUM	.05 to 1
CHLORIDE	
LAURYL HYDROXYETHYL IMIDAZOLINE	5 to 50
100%	
SODIUM POTASSIUM	20
ALUMINOSILICATE A3	
ADDITIVES	.01 to 5

TABLE I

COMPOSITION	WET COMBING TOTAL ENERGY mi	WET COMBING MAX LOAD G FORCE
EXAMPLE1	12.97	14.48
EXAMPLE 2	11.93	12.97

5 The above table I demonstrates that compositions of the invention which comprise molecular sieves (example 2) have the same or even better wet combing properties than compositions without sieves (example 1) and that therefore, the compositions of the invention have the same or even better conditioning properties than compositions without molecular sieves.

- 23 -

Table II

Summary of Self Warming Compositions-Effect of Molecular Sieve Addition

WT. % PORE SIZE WATER COMPOSITION IN ANG. MOL. DILUTION SIEVES TEMP. IN STROMS DEGREES C1 NA² 0 응 +8 100% PEG 200 0% 0 NA 100% GLYCERIN 10% +11 3 90% PEG 200 +10%ALDRICH ЗА 10왕 3 90% GLYCERIN +10% ALDRICH +6 ЗА 10% 9-10 +10 90% PEG 200 9+10% ALDRICH 13X4 +9 9-10 10% 90% GLYCERIN +10% ALDRICH 13X 10% 90% PEG 200 +10% ZEOLEX 35-+10 NA P^5 10왕 0 NA 90% GLYCERIN +10% ZEOLEX 35-P 90% PEG 200 +10% SYLOSIV 3A3 +19 10왕 10% 3 90% GLYCERIN +10%SYLOSIV 3A +11 0% CONDITIONER EXAMPLE 1 +7 Na (Comparative example without molecular sieves) +18 3 20% CONDITIONER EXAMPLE 2 15% +11 3 CONDITIONER EXAMPLE 3 +18 20% CONDITIONER EXAMPLE 4

5

DUODOOID, 340 000000144 1 -

TABLE NOTES

5

- 1) Water dilution temp increase is the change in temperature in degrees C when 70 parts of composition is mixed with 30 parts of water.
- 2) NA is not applicable.
- 3) Sylosiv 3A is a tradename of the molecular sieves supplied by WR Grace.
- 4) Aldrich 13X and Aldrich 3A are tradenames of molecular sieves supplied by Aldrich Chemical.
- 5) ZEOLEX 35-P is a tradename of amorphous sodium aluminosilicate supplied by JM Huber.
- The above table 11 demonstrates that compositions of the invention (examples 2,3,4) raise temperature on mixing with water significantly more degrees C than compositions without molecular sieves and microporous materials (example 1). In addition it demonstrates the need for appropriate selection of microporous materials with carrier

- 25 -

CLAIMS

5

10

DISCOURT AND AMBROARAS I

- 1. A hair conditioner composition which is essentially anhydrous that comprises:
 - (a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule;
 - (b) carrier molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials; and
 - (c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials.
- 2. A composition according to claim 1 wherein the microporous ingredient is an inorganic salts such as crystalline metal silicates selected from the group consisting of sodium aluminum potassium silicate, aluminum silicate, calcium aluminum silicate, activated alumina
 (aluminum oxide), diatomaceous silicas, bentonites, aluminum oxides, silicon oxides, and crystalline metal aluminosilicates.
- 3. A composition according to claim 2 wherein the
 25 microporous material is an aluminosilicate which ranges in
 average pore size from about 3 Angstroms to about 10
 Angstroms.
- A composition according to claim 1 wherein the
 microporous material is an activated charcoal.

5. A composition according to claim 1 wherein the carrier material is selected from the group consisting of hydrophilic glycols, polyethylene glycols, glycerin, and a polar solvent.

5

- 6. A composition according to claim 5 wherein the hydrophilic glycol is selected from the group consisting of propylene glycol, ethylene glycol, hexylene glycol, glycerin, sorbitol, butanediol, butylene glycol, and mixtures thereof.
- 7. A composition according to claim 5 wherein the polyethylene glycol is selected from the group consisting of PEGs -4, -6, -8, -9, -10, -12, -14, -16, -18, -20, -200, -400 and -600; beheneth -5 and -1 0; PEG-7 betanaphthol and 15 PEG-1 5 butanediol; buteth-3 carboxylic acid, butoxynol-5 and -19, PEG-8 C12-18 ester, C12 -13 pareth-7 carboxylic acid, Cl 1 -15 pareth-7 carboxylic acid, Cl2 -15 pareth-7 carboxylic acid, C14 -15 pareth-8 carboxylic acid, PEG-8 20 caprate, PEG-8 caprylate, PEG-8 caprate/caprylate, PEG-6, and -8 caprylic/capric glycerides, capryleth -6 and -9 carboxylic acids, PEG-8 caprylatep; ceteareth -2, -3, -4, -5, -5, -6, -7, -8, -10, -11, -12, -13, -15, -6, -17, -18, and -20; choleth -1 0 and -20; PEG-3 cocamide, PEG-5 cocamide, PEG-6 cocamide, PEG-7 cocamide, PEG-1 1 cocamide, 25 PEG-20 cocamide; PEG-2 cocamine, PEG-3 cocamine, PEG-5 cocamine, PEG-1 0 cocamine, PEG-1 5 cocamine, and PEG-20 cocamine; PEG-5 cocoate, PEG-8 cocoate, PEG-15 cocoate; coceth-3, 5, and -8; PEG-2 dilaurate, PEG-4 dilaurate, PEG-6 30 dilaurate, PEG-8 dilaurate, PEG-12 dilaurate, PEG-20 dilaurate, PEG-4 dioleate, PEG-6 dioleate, PEG-8 dioleate,

PEG-1 0 dioleate, PEG-12 dioleate, isosteareth-2, isosteareth-3, isosteareth-10, isosteareth-12, isosteareth-20; isoceteth-10, and -20; isodeceth -4, -5, and -6; isostereath -2, -3, 1 0, 12, and -20; PEG-3 lauramine oxide; PEG-2 laurate, PEG-4 laurate, PEG-6 laurate, PEG-8 laurate, PEG-9 laurate, PEG-10 laurate, PEG-12 laurate, PEG-14 laurate, and PEG-20 laurate; laureth -1, -2, -3, -4, -5, -6, -7, -8, -9, -10, -11, -12, -13, -14, -15, 16, and -20; oleth 2, -3, -4, -5, -6, -7, -8, -9, -10, 12, -15, -16, and -20; stereath -2, -3, -4, -5, -6, -7, -10, -11, -13, -14, -15, -16, and -20; and trideceth -3, -5, -6, -9, -10, -11, -12, and -15.

- 8. A composition according to claim 5 wherein the polar solvent is selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, isopropanol and mixtures thereof.
- 9. A composition according to claim 1 wherein the
 20 conditioner materials are selected from the group consisting
 of quaternary ammonium compounds, amidoamines, hydrophilic
 silicones, cationic polymers, hydrocarbons, fatty alcohols,
 and mixtures thereof.
- 10. A composition according to claim 9 wherein the silicone is selected from the group consisting of a polyalkyl siloxane, a polyaryl siloxane, a polyalkylaryl siloxane and mixtures thereof.
- 30 11. A composition according to claim 10 wherein the silicone is selected from the group consisting of a volatile

- 28 -

siloxane such as cyclotetrasiloxane, cylopentasiloxane, cyclohexasiloxane, or mixtures thereof.

12. A composition according to claim 1 0 wherein the silicone is a group of nonvolatile silicones consisting of dimethicone, dimethiconol, amodimethicone, phenyltrimethicone, silicone copolyol, and mixtures thereof.

. 5

- 13. A composition according to claim 9 wherein the cationic polymer is selected from the group consisting of: Guar hydroxypropyltrimonium chloride, poly(dimethyidiallylammonium chloride), poly(dimethyl butenyl ammonium chloride) bis (triethanolammonium chloride), Poly (dipropyldiallylammonium chloride), Poly (methylbeta propaniodiallylammonium chloride), Poly (diallylpiperidinium chloride), Poly (vinylpyridinium chloride), quaternised poly(dimethylaminoethylmethacrylate) and mixtures thereof.
- 14. A composition according to claim 9 wherein the hydrocarbon is selected from the group consisting of nonane, octane, heptane, tert-pentane, dodecane, decahexane, decane, heptadecane, trimethylheptane, trimethylhexane, 4methylheptane, 4-methyldecane, isobutane, isopentane, isooctane, hexane, isododecane, isohexadecane, and mixtures thereof.
- 15. A composition according to claim 9 wherein the quaternary ammonium compound is selected from the group consisting of lauratrimonium chloride, quaternium -1 6, lauralkonium chloride, dicetyldimonium chloride, distearyl

- 29 ~

dimonium chloride, behenyl dimonium chloride, cetylpyridinium chloride, soyatrimonium chloride, myristyltrimonium chloride, cetrimonium chloride, PEG-2 cocomonium chloride, PEG 2 cocoyl quaternium -4, PEG-2 oleyl quaternium-4, polyquaternium -6,-7, -11, -5, -24, and mixtures thereof.

- 16. A composition according to claim 14 wherein the amidoamine is selected from the group consisting of diethylaminoethylstearamide, isosteamidopropyldimethylamine, cocamidopropyldimethylamine, ricinoleamido propyldimethylamine, oleamidopropyldimethylamine, behenamidopropyldimethylamine, palmitamidopropyldimethylamine, searamidylethyldiethylamine, soyamido propyidimethylamine and dimethylaminopropyl myristamide, stearamidylpropyl dimethylamine.
- 17. A composition according to claim 9 wherein the fatty
 20 alcohol is selected from the group consisting of stearyl
 alcohol, cetyl alcohol, behenyl alcohol, myristle alcohol,
 coco alcohol, and mixtures thereof.
 - 18. A composition according to claim 1 which comprises:

25

INGREDIENT	WEIGHT %
PEG 200 5	50.45
CETEARYL ALCOHOL 2	2.5
5 BEHENTRIMONIUM CHLORIDE 2	2.0
STEARETH-2	1.0
STEARETH-21	1.0
PANTHENOL	0.1
GLYCERIN	18.6
10 CITRIC ACID	0.7
DIMETHICONE	3.0
SODIUM POTASSIUM ALUMINO- 2	20.0
SILICATE 3 Angstroms	
FRAGRANCE	0.65

15

19. A method for conditioning hair with self warming which comprises applying to said hair an effective amount of a composition according to claim 1 and then applying to the hair water.

20

20. A method for conditioning hair with self warming which comprises applying to said hair water, and then applying to the hair an effective amount of a composition according to claim 1.

- 21. A hair shampoo composition which is essentially anhydrous that comprises:
- (a) one or more microporous materials each of which

 has an average pore size larger than the critical diameter of a water molecule;

- 31 -

- (b) carrier molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials; and
- 5 (c) shampoo molecules or molecular aggregates that have critical diameters larger than the average largest pore size of the microporous materials.
- 22. A method for shampooing hair with self warming which
 comprises applying to said hair water, and then applying to
 the hair an effective amount of a shampoo composition
 according to claim 21.
- 23. A method for shampooing hair with self warming which
 comprises applying to said hair an effective amount of a
 shampoo composition according to claim 21, and then applying
 to the hair water.
- 24. A hair shampoo and conditioner composition which is essentially anhydrous that comprises:

- (a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule;
- 25 (b) carrier molecules or molecular aggregates that have critical diameters larger than the average largest pore size of the microporous materials; and
 - (c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials;

- (d) shampoo molecules or molecular aggregates that have critical diameters larger than the average largest pore size of the microporous materials.
- 5 25. A method for shampooing and conditioning hair with self warming which comprises applying to said hair water, and then applying to the hair an effective amount of a shampoo and conditioner composition according to claim 24.
- 26. A method for shampooing and conditioning hair with self warming which comprises applying to said hair an effective amount of a shampoo and conditioner composition according to claim 24, and then applying to the hair water-
- 15 27. A composition in accordance with claim 1, wherein the average pore size is from about 3 Angstroms to about 13 Angstroms.
- 28. A composition in accordance with claim 1, wherein the average pore size is from about 3 Angstroms to about 10 Angstroms.

Ir. ational Application No PCT/EP 99/10168

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A61K7/00 A61K A61K7/06 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) IPC 7 A61K Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Category 3 Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. P,X EP 0 897 719 A (UNILEVER PLC ; UNILEVER NV 1-3,5-719,27,28 (NL)) 24 February 1999 (1999-02-24) page 6, line 45,46 claims 1,6; example 1 US 3 702 302 A (WILSON VERNON COLUMBUS) X 1-3,5,7, 27,28 7 November 1972 (1972-11-07) column 3, line 1-30 column 4, line 1-30 column 4, line 47-54 X EP 0 586 929 A (KAO CORP) 1-3,5-7,16 March 1994 (1994-03-16) 9,10,12, 15,19, 27,28 claims 1,17; example 4 -/--Further documents are listed in the continuation of box C. Patent family members are listed in annex. Χ X Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-"O" document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled in the art. document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 17 April 2000 11/05/2000 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Sierra Gonzalez, M Fax: (+31-70) 340-3016

It lational Application No

Category °	ation) DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages	
	of the relevant passages	Relevant to claim No.
A	H.F. MARK: "KIRK - OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. vol 15" 1978 XP002133448 page 638 -page 660; table 6	1-20,27, 28
A	H.F. MARK: "Kirk-Othmer Encyclopedia of Chemical Technology" XP002133449 page 115 page 122-124	1-20,27, 28
A	H.F. MARK: KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, vol. 1, 1978, pages 563-564, XP002133655	1-20,27, 28

international application No.

PCT/EP 99/10168

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. X Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically: See FURTHER INFORMATION SHEET PCT/ISA/210
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest The additional search fees were accompanied by the applicant's protest. No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-17, 19-20 and 27-28 (partially); 21-26 (not searched)

Present claims 1-17 and 19-20 and 27-28 relate to a composition defined by reference to the following parameters of the constituent compounds:

P1: critical diameter of the water molecule P2: average pore size of microporous materials

P3: critical diameter of the carrier molecules P4: critical diameter of the conditioner molecules

and by the following ratios:

P2/P1 P3/P2 P4/P2

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible.

Furthermore, the term "molecular aggregates" is obscure. It has not been disclosed in the application in a manner sufficiently clear and complete to allow the skilled man to understand the application (Article 5 PCT). It is doubtful whether the critical diameter refers to the molecule or to the molecular aggregate.

Moreover, the term "shampoo molecules" of claims 21-26 it is not usual in the art and it is not clear to the skilled person. It also has not been disclosed in the application in a manner sufficiently clear and complete to allow the skilled person to understand the application (Article 5 PCT). As a consequence and considering also the above mentioned objections to clarity (to the parameters and to the term "molecular aggregate") a meaningful search of these particular claims is considered to be impossible. Claims 21-26 have not been searched.

Consequently, the search has been restricted to a composition comprising one or more microporous materials (as defined in the description, page 5, line 10-page 6, line 7), carrier molecules (as defined on page 6, line 26-page 8, line 16) and conditioner molecules (as defined on page 8, line 22-page 13, line 11), as defined completely in the claims with due regard to the general idea underlying the application.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is

FU	RTHER INFORMATION CONTINUED FROM PCT/ISA/ 210
	the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.
	•

Information on patent family members

Ir. ational Application No PCT/EP 99/10168

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0897719	Α	24-02-1999	CA 2244591 A JP 11116463 A	19-02-1999 27-04-1999
US 3702302	Α	07-11-1972	NONE	
EP 0586929	A	16-03-1994	DE 4227203 A DE 9211006 U AT 110955 T DE 69300008 D DE 69300008 T JP 7069835 A US 5538720 A	07-10-1993 16-12-1993 15-09-1994 13-10-1994 26-01-1995 14-03-1995 23-07-1996